BIO-OIL PRODUCTION FROM OIL PALM STEM USING FLUIDIZED BED REACTOR

By

Mohd Aizudin Aizat bin Mohd Zainudin

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)
SEPTEMBER 2011

Universiti Teknologi PETRONAS,
Bandar Seri Iskandar,
31750 Tronoh,
Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

BIO-OIL PRODUCTION FROM OIL PALM STEM USING FLUIDIZED BED REACTOR

By

Mohd Aizudin Aizat bin Mohd Zainudin

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Prof. Dr. Yoshimitsu Uemura)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2011

Table of Contents

Table of Figure

List of Table

ABSTRACT

Oil palm is one of the major economic crops in many countries. Malaysia alone produces about 47% of the world's palm oil supply and can be considered as the world's largest producer and exporter of palm oil. Malaysia also generates huge quantity of oil palm biomass including oil palm trunks, oil palm fronds, empty fruit bunches (EFB), shells and fibers as waste from palm oil fruit harvest and oil extraction processing. This study presents an investigation on the production of bio-oil from biomass by fast pyrolysis process. Oil palm stem with the fraction size of 0.15 – 5 mm was utilized in this study. In this work, fast pyrolysis of oil palm stem was carried out in a fluidized bed fast pyrolysis unit under nitrogen gas flowrate of 1.32 m3/h, with reactor temperature of 450 °C. The fluidized bed fast pyrolysis unit has six successive condensers. Thus, six fractions of bio-oil samples were acquired from the six condensers and each of them were characterized in term of moisture content, calorific value, ash content and element content. The bio-oil yield was 11% and the highest calorific value among the six bio-oil samples was 16.2 MJ/kg. The chemical characterization and calculation of residence time showed that the condition of pyrolysis in this experiment is not favorable in producing bio-oil, however effective to produce bio-char.

CHAPTER 1

1. INTRODUCTION

1.1 Background of Study

The world's energy consumption, especially in the transportation sector is still dependent on fossil fuels (J.P Dorian et al. 2006). This leads to serious energy crisis and environmental problems, i.e. fossil fuel depletion and pollutant emission. The increasing energy demands will speed up the exhaustion of the finite fossil fuel. Moreover combustion of fossil fuel produces substantial greenhouse gases (GHG) and toxic gases such as CO2, CH4, SO2, NOx and other pollutants, causing global warming and acid rain (M.Ni et al. 2006). It is important to develop suitable long-term strategies based on utilization of renewable fuel that would gradually substitute the declining fossil fuel production; the alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available (P.Westermann et al. 2007).

Biomass is one of the most abundant renewable resources; it is formed by fixing carbon dioxide in the atmosphere during the process of plant photosynthesis and, therefore, it is carbon neutral in its lifecycle. Biomass provides a clean, renewable energy source that could dramatically improve the environment, economy and energy security. At present the palm oil industry generates large volume of biomass from the oil extraction process such as mesocarp fiber, shell, empty fruit bunch (EFB) and palm oil effluent (POME). The world annual production of oil palm residues amounts to 184 million tonnes. About 53 million tonnes of residues are produced from oil palm trees every year in Malaysia alone, and it is increasing annually by 5%.

Oil palm fronds can be used for fuel or energy production by fermentation or thermal conversion such as pyrolysis, gasification and combustion. Among the thermal conversion processes of biomass, pyrolysis can be used either as an independent process for fuels and other valuable chemical products, or as an initial step to gasification and combustion. By thermal decomposition of biomass components in the absence of oxygen, pyrolysis yields carbon-rich char, condensable vapors and non-condensable

gases. Bio-oil refers to the dark brown liquid from pyrolysis of biomass after condensing the pyrolysis vapors that contain over 300 compounds (Czernik and Bridgwater, 2004; Lee et al., 2008; Park et al., 2008b, 2010a).

Pyrolysis is a promising thermochemical technology to obtain char, gas and liquid fuels, this technology known since the earliest stages of human technology. The proportion of the products depend on the pyrolysis technique used and pyrolysis parameters such temperature, heating rate, particle size, etc. Slow pyrolysis occurs a long period of time and favors char yields whereas fast pyrolysis occurs in short reaction times and favors high liquid yields (Horne and Williams, 1996). Much of the present interest in pyrolysis focuses to obtain maximum oil yields. These obtained liquid products are called as bio-oils, bio-fuels or bio crudes. They have many advantages such as lower content of nitrogen or sulfur, having high energy density and easier handling comparing with raw material (Agblevor et al., 1995). In this study, oil palm stem was pyrolysed above minimum fluidization velocity in a fluidized bed reactor and the products obtained were characterized.

1.2 Problem statement

Biomass offers much potential as a renewable fuel for displacing coal in large-scale power plants. Given that the carbon contained in biomass is taken directly from the atmosphere, the fuel is largely considered to be carbon-neutral. Biomass also contains less sulfur, nitrogen, ash, and heavy metals than coal.

However, there are currently several problems with biomass that prohibit it from being used on a larger scale for power production. It has a much lower heating value compared to coal and suffers from logistical issues related to transportation, handling, and storage. Because of high moisture contents and low energy densities, the cost of transportation to the plant is high.

This study examine the pyrolysis of oil palm stem in a fluidize bed reactor to produce bio-oil. Pyrolysis process produced bio-oil as its primary product and said to be well

suitable material to replace crude oil. In order for bio-oil to become fuel replacement, an investigation on bio-oil properties and chemical compound in bio-oil had to be determined to find the effectiveness and suitability a new energy source.

1.3 Objective

1 To produce bio-oil from oil palm stem
2 To analyze the characteristic of bio-oil produced.
3 To calculate the minimum fluidization velocity

1.4 Scope of Study

The scope of this study is to use palm oil waste as the biomass source which is stem part. The most abandon biomass in Malaysia come from the palm oil plantation. With production of billion ton per annum, palm oil waste can be a great source for pyrolysis process in producing bio-oil.

The pyrolysis process is conducted in a fluidized bed reactor under nitrogen gas flowrate of 22 l/min with reactor temperature of 450°C.

The critical step before the process of bio-oil production is the sample preparation, where the feedstocks (oil palm stem) will be

1) dried to typically less than 10% in order to minimise the water in the product liquid oil.

2) grinded and sieved into particles sizes which is 0.15 – 0.5 mm to ensure rapid pyrolysis reaction.

3) characterized their properties in terms of: moisture content, calorific value, ash content and element content (carbon, hydrogen and nitrogen).

The final step of bio-oil production is to characterize the properties of bio-oil.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Bio-oil from Pyrolysis

Bio-oil is renewable, which is produced from biomass through a process known as fast pyrolysis. Fast pyrolysis represents a potential route to upgrade the biomass to value added fuels and renewable chemicals. There is an urgent need to develop a sustainable energy supply as the impact of burning fossil fuels on our climate is becoming even more obvious and the availability of fossil fuels is decreasing. Bio-oil contributes to the reduction of greenhouse gas emissions and it offers several advantages, as it is easy to use, store, and transport. Bio-oil that can be extracted from dried biomass including dried oil palm wastes is currently under investigation as a substitute for petroleum. Bio-oil contains fragments of cellulose, hemicelluloses, lignin, and extractives and they are typically brown liquids with a pungent odor. For woody feedstock, temperatures around 500 °C together with short vapor residence times are used to obtain bio-oil yields of around 70%, and char and gas yields of around 15% each (Heo et al.2010). Bio-oil is a high-density oxygenated liquid, which can be burned in diesel engines, turbines or boilers, though further work is still required to demonstrate long-term reliability. It is also used for the production of speciality chemicals, currently mainly flavourings.

2.2 Biomass Decomposition by Thermo-chemical Processes

The main routes for biomass conversion into energy are bio-chemical/biological processes and thermo-chemical processes. The first routes are attractive due to lower secondary pollution generated from microorganism conversion method; however, major

drawbacks from these processes are difficult to culture microorganism, low efficiency and higher operating temperature needed to operate. Fig. 1 demonstrates the energy production technologies based on biomass (Mohammed et al. 2011).

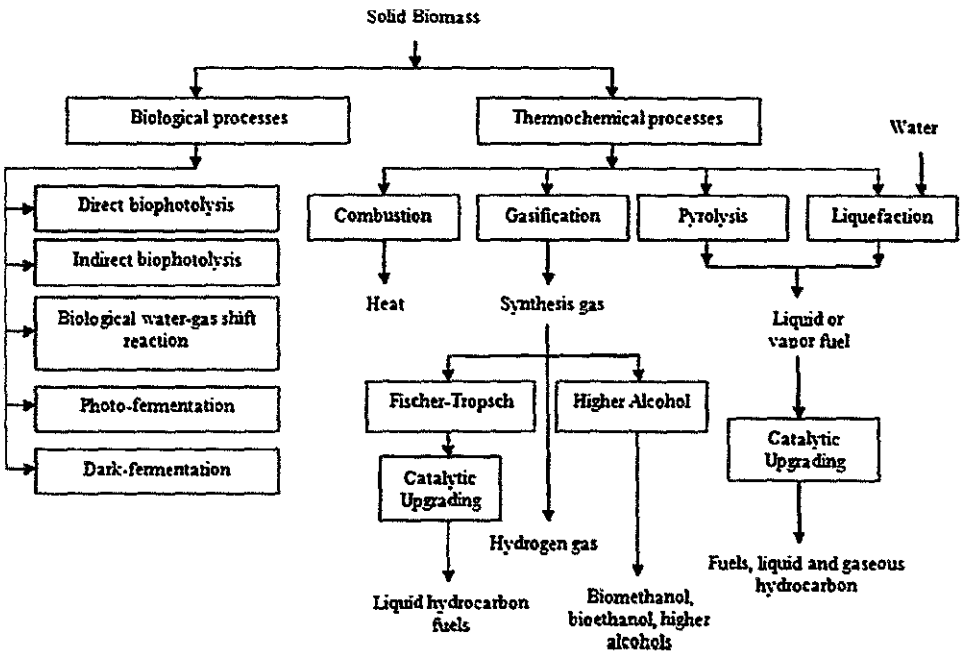

Figure 1: demonstrates the energy production technologies based on biomass

2.3 Pyrolysis

Pyrolysis is a conversion of biomass to liquid, solid and gas mixture by direct thermal decomposition of the biomass in the absence of oxygen at temperature range of 350–550 °C (L,J et al. 1999). The pyrolysis processes under development are based on two different concepts namely slow pyrolysis and fast or flash pyrolysis. These differ from each other in terms of chemistry, yields and quality of products. Liquids produced from pyrolysis are called bio-oil; it is a complex mixture of aliphatic and aromatic compounds (D. Meier and O. Faix et al. 1998). Pyrolysis reaction is an endothermic reaction as shown below:

biomass+heat→bio-oil+gas+char

The product distribution obtained from different modes of pyrolysis process are summarised in the table below. Fast pyrolysis for liquids production is of particular interest currently as the liquids are transportable and storage.

Table 1: Typical product yields (dry wood basis) obtained by different modes of pyrolysis of wood

Mode	Condition	Liquid	Char	Gas
Fast	~500°C,Short hot vapour residence time ~1s	75%	12%	13%
Intermediate	~500°C, hot vapour residence time ~10-30s	50%	25%	25%
Slow-Torrefaction	~290°C, solid residence time ~30s	-	82% solid	18%
Slow-Carbonization	~400°C, long vapour residence time ~hrs→days	30%	35%	35%
Gasifiaction	~800°C	5%	10%	85%

Fast pyrolysis occurs in a time of few seconds or less. Therefore, not only chemical reaction kinetics but also heat and mass transfer processes, as well as phase transition phenomena, play important roles. The critical issue is to bring

the reacting biomass particle to the optimum process temperature and minimize its exposure to the intermediate (lower) temperatures that favour formation of charcoal. One way this objective can be achieved is by using small particles, for example in the fluidised bed processes that are described later. Another possibility is to transfer heat very fast only to the particle surface that contacts the heat source, which is applied in ablative processes.

2.4 Reactor for pyrolysis.

a) Bubbling fluid beds

Bubbling fluid beds, usually referred to as just fluid beds as opposed to circulating fluid beds (see below) have the advantages of a well understood technology that is simple in construction and operation, good temperature control and very efficient heat transfer to biomass particles due to high solids density. A typical configuration is shown below with electrostatic precipitators that are more widely used in laboratory systems. Commercial plants may try to rely on a series of collection stages including de-misters although aerosol capture is notoriously difficult.

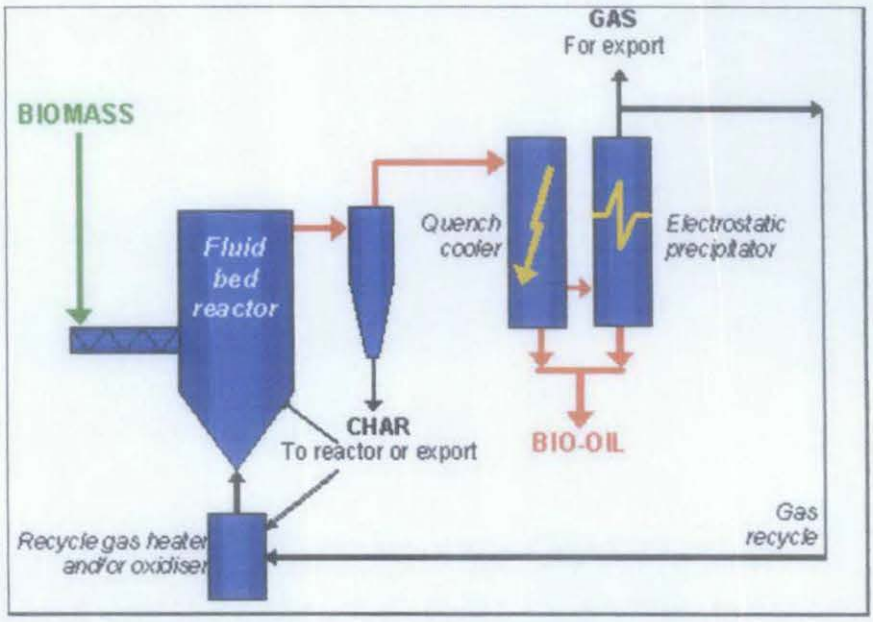

Figure 2: Bubbling fluid bed reactor with electrostatic precipitator

Heating can be achieved in a variety of ways as shown in the figure below and scaling is well understood. However, heat transfer to bed at large-scales of operation has to be considered carefully due to scale-up limitations of different methods of heat transfer.

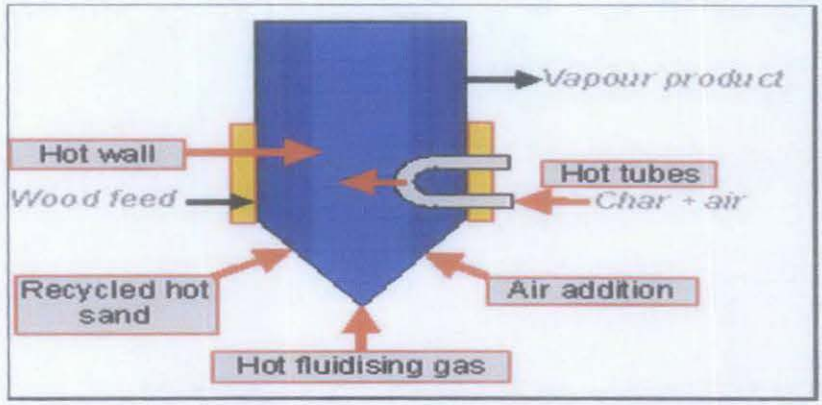

Figure 3: Methods of heat transfer to a pyrolysis reactor

.

Fluid bed pyrolysers give good and consistent performance with high liquid yields of typically 70-75%wt. from wood on a dry feed basis. Small biomass particle sizes of less than 2-3 mm are needed to achieve high biomass heating rates, and the rate of particle heating is usually the rate limiting step. Residence time of solids and vapours is controlled by the fluidising gas flow rate and is higher for char than for vapours. As char acts as an effective vapour cracking catalyst at fast pyrolysis reaction temperatures, rapid and effective char separation/elutriation is important. This is usually achieved by ejection and entrainment followed by separation in one or more cyclones so careful design of sand and biomass/char hydrodynamics is important.

2.5 Properties of Pyrolysis Feedstock

Oil palm fronds are available daily throughout the year when the palms are pruned during the harvesting of fresh fruit bunches. The fronds are left rotting on the palm oil trees, mainly for soil conversion, erosion control and ultimately the long-term benefit of nutrient recycling (Park et al. 2004). Oil palm trunk is obtained during the re-plantation of the oil palm trees. EFB, mesocarp fiber (MF) and shells are collected during the pressing of sterilized fruits .

The chemical and physical properties of oil palm biomass vary according to their diverse origins and plant species. Generally cellulose, hemicelluloses, lignin and ash are the major oil palm biomass components. Table 2 tabulates the chemical composition of oil palm biomass (Mohammed et al. 2011).

Table 2: Chemical composition of oil palm biomass

Component	Oil palm biomass chemical composition (wt %)				
	EFB	Shell	Frond	Fiber	Trunk
Cellulose	38.3	20.8	49.8	34.5	37.14
Hemicelluloses	35.3	22.7	83.5	31.8	31.8
Lignin	22.1	50.7	20.5	25.7	22.3
Ash	1.6	1.0	2.4	3.5	4.3

Biomass fuels are characterized by what is called the "Proximate and Ultimate analyses". The "proximate" analysis gives moisture content, volatile content (when heated to 950 C), the free carbon remaining at that point, the ash (mineral) in the sample and the high heating value (HHV) based on the complete combustion of the sample to carbon dioxide and liquid water (Manoj Khandelwal et al. 2011) . The low heating value, LHV, gives the heat released when the hydrogen is burned to gaseous water, corresponding to most heating applications and can be calculated from the HHV and H2 fraction. The "ultimate" analysis" gives the composition of the

biomass in wt% of carbon, hydrogen and oxygen (the major components) as well as sulfur and nitrogen (if any).

Ultimate and proximate analysis of biomass sample need to be carried out, and must be according to standard methods of waste quality. In one experiment using furniture sawdust as a feedstock, ultimate analysis was carried out using an automatic elemental ana-lyzer (Flash EA 1112 Series CHNS-O analyzer, CE Instrument) and proximate analysis was performed. Each test case was repeated in triplicate and the average results were taken (Heo et al. 2010). Table 3 below show ultimate and proximate analyses of the waste furniture sawdust (Heo et al. 2010).

Table 3: ultimate and proximate analyses of the waste furniture sawdust

Ultimate analysis		Proximate analysis	
Component	Content (wt %)	Component	Content (wt %)
C	49.1	Moisture	9.1
H	6.2		
N	3.0	Combustible	91.9
O	41.7	Ash	-
S	-		

a) Pyrolysis Product analysis.

For the experiment using waste furniture sawdust in fluidized bed, the char was separated from the bed and the cyclone to determine its yield. The pyrolysis gases at the downstream of the electrostatic precipitator were analyzed using a GC-TCD and GC-FID (ACME 6000, Young Lin Instruments Co., Ltd.). Using the accumulated flow rate and the composition of the gas, its mass yield was determined. The bio-oil was collected from the condensers and the electrostatic precipitator. Since the viscous organic fraction in the electro-static precipitator was very difficult to fully separate, the oil yield was calculated by difference, using

the char and gas yields. The bio-oil that was produced was in a heterogeneous state, with aqueous and heavy organic fractions. Both the chemical and physical analyses of the bio-oil, however, were required to be in the homo-geneous state. To acquire representative samples, two bio-oil samples were taken from the 10–20 vol.% parts of the top and bottom sections after sufficient stirring.

Bio-oil is also known as pyrolysis oil. The product of bio-oil will be kept in freezer before analysis. The water content of bio-oil was determined by the Karl–Fischer titration (KF DL31 from Mettler-Toledo) using aquastar CombiTitrant 5 keto (from Merck) as titrant (Jun Shen et al). The content of lignin derived oligomers was measured by their precipitation in cold water. Briefly, 3 g of bio-oil was injected in droplets into 300 mL of ice-cooled water under strong agitation at a rate of 1000 rpm.

Bio-oil is characterized using UV-fluorescence spectroscopy (Jun Shen et al). Bio-oil solution of 3.5 ppm were prepared by diluting the bio-oil samples with methanol The chemical composition of bio-oil is important since it may give approaching into its quality, stability or suitability for downstream upgrading. In this experiment conducted by Jun Shen et al. the thermogravimetric analysis of bio-oils was carried out by heating the bio-oil in nitrogen with a flow rate of 20 mL min1 in a Perkin–Elmer Pyris 1 TGA. Thermogravimetric Analysis (TGA) measures weight changes in a material as a function of temperature (or time) under a controlled atmosphere. Its principal uses include measurement of a biomass thermal stability and composition. The viscosity of bio-oil also was determined with a Brookfield Syn-cro-Lectric viscometer (model LVT). All measurements were taken at room temperature (23 ± 2°C), in a coaxial cylinder geometry (L,J et al. 1999).

2.6 Pyrolysis Products Application

Bio-oil can substitute for fuel oil or diesel in many static applications including boilers, furnaces, engines and turbines for electricity generation. The possibilities are summarised in the figure below. There is also a range of chemicals that can be extracted or derived including food flavourings, specialities, resins, agri-chemicals, fertilisers, and emissions control agents. Upgrading bio-oil to transportation fuels is feasible but currently not economic (M.Ni et al. 2006).

Char can be utilized for many industrial purposes. For instance, char is used as solid fuel in boilers where biomass is previously burnt to produce energy to support the operating of the boilers. Other than that, char can be used for the production of activated carbon (M.Ni et al. 2006).

Pyrolysis gas containing significant amount of carbon dioxide and methane that can be used for industrial combustion usages (M.Ni et al. 2006).

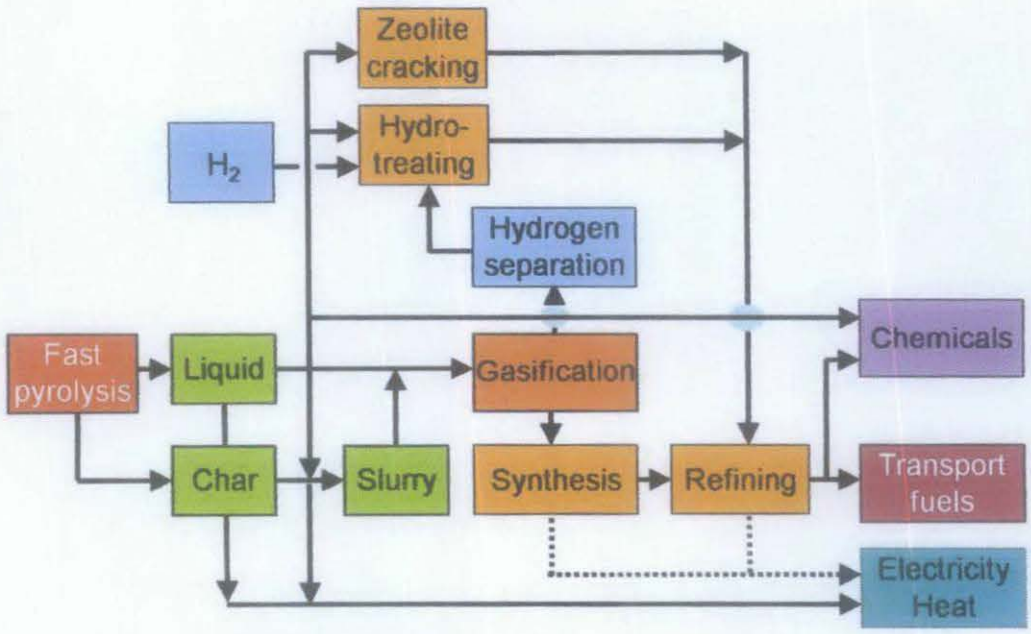

Figure 4:Applications for Bio-oil.

CHAPTER 3

3. MATERIALS AND METHODS

3.1 Raw material

Oil palm frond was used as feedstock for bio-oil production in this study. An oil palm frond of about 10 kg was collected from FELCRA Nassaruddin palm oil mill located in Bota, Perak. The frond was cut into smaller pieces and dried at 105°C. The fronds were manually chopped into smaller pieces so that they could be fed into grinding machine. The frond was separated into leaf part and stem part. It was then grind, sieved and separated in fractions using the test sieve shaker. The separated portion particle size was 0.15- 0.5mm.

Characterization of the oil palm frond includes proximate analysis, calorific value and elemental analysis. The proximate analysis was used to determine the moisture content, volatile matter, fixed carbon and ash content in oil palm fronds. The calorific value of the frond was determined using a bomb calorimeter.

3.2 Biomass Feedstock Characterization

3.2.1 Moisture content analysis.

This analysis is to measure the moisture content in the feedstock. Moisture content analysis is referred to ASTM E 871 – 82. The feedstock was dried in drying oven for 24 hours (plus 1 hour until hour 27) with the temperature of 105 °C. The moisture of content the feedstock was determined by equation 1:

$$\text{Moisture content} = \frac{W_{Biomass} - W_{Biomass@27}}{W_{Biomass}} \times 100\ \%$$

3.2.2 Ash content analysis

Total amount of minerals present within the feedstock was determined using ash content analysis. This analysis is referred to ASTM E 1755 – 95. The feedstock was heated in furnace for 3 hours with the temperature of 700 °C. The ash content of feedstocks was determined by equation 2:

$$\text{Ash content} = \frac{W_{ash}}{W_{Biomass}} \times 100\ \%$$

3.2.3 Calorimetry analysis

The calorific value of oil palm frond was determined using a bomb calorimeter C5003 IKA-Werke. The test procedure consists of oil palm frond weighting (0.3-0.4 g), installing a fuse and charging the bomb with oxygen. Caloric value is the amount of energy release when a feedstock is completely combusted under specific condition.

3.2.3 Elementary analysis

This analysis is to determine the composition of carbon, hydrogen and nitrogen contents in oil palm frond. The composition were determine by using CHN 2400 Perkin Elmer. First, a silver capsule (502-206) was tare and sample is added. Next, the capsule was crimp and folded. The weight was recorded. Noted that, the weight must in between 1.0

to 2.0 mg. CHNS 2400 Perkin Elmer will analyze and the CHNS value will appear on screen.

3.3 Experimental Setup

3.3.1 Fast Pyrolysis Process (Bio-oil Production)

The experimental setup used for this study consists of three main parts which are:

3.3.2 A fluidized bed reactor made of stainless steel with a diameter of 108 mm and a length of 763 mm installed with four electric jacket heaters with PID controllers to raise and maintain temperature at a desired level.

3.3.3 A screw feeder for feeding biomass feedstock particles to the reactor.

3.3.4 Two cyclones and six condensers at downstream. The two cyclones are installed successively for removing the char from the reaction mixture flowing out from the reactor.

Pyrolysis of oil palm frond (stem and leaf) was carried out using a fluidized bed reactor. A weighted sample of grinded biomass is introduced into the reactor.. The fluidization medium was silica sands with the average diameter and the bulk density are 0.15 – 0.25mm and 1448kg/m^3 respectively. There are also three stages of condensation in this unit which are using three different medium; (1) using tap water at room temperature, (2) chilled water at 10 °C and (3) glycol at -10 °C. The purpose of these three stages of condensation is to gradually condense the hot stream to form bio-oil at optimum production. The six condensers are for removing the liquid product thoroughly from the reaction mixture flowing out from the second cyclone. This process was operated at atmospheric pressure.

The whole experimental rig that consists of the volatiles and gas collection system is as illustrated in the fig 5.

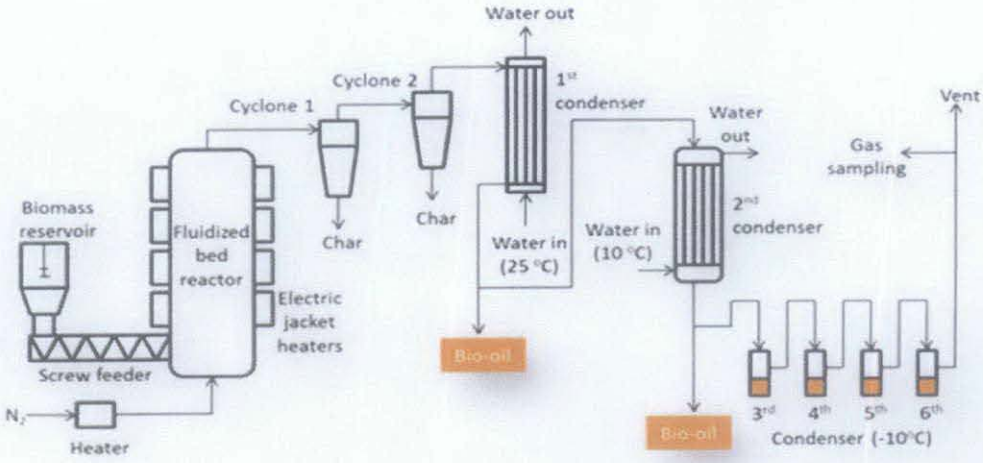

Figure 5: Experimental setup for producing bio-oil

Figure 6: Continuous fluidized-bed fast pyrolysis unit

Table 4:Description of the continuous fluidized-bed fast pyrolysis unit

No.	Description
1	Control panel
2	Hooper
3	Screw feeder
4	Heater
5	Continuous fluidized-bed reactor
6	Cyclone 1
7	Cyclone 2
8	Heat exchanger (medium: tap water at room T)
9	Shell and tube condenser (medium: chilled water at 10°C)
10	Table top cooling bath (medium: glycol at -10°C)
11	Char collector 1
12	Char collector 2
13	Bio-oil collector 1
14	Bio-oil collector 2
15	Bio-oil collector 3 (inside the table top cooling bath)
16	Gas collector
17	Flowmeter
18	Nitrogen in

3.4 Products Characterization

The products (bio-oil, char and gas) will be collected and the properties of each component will be determined using a few analysis techniques as per following.

A) Bio-oil

- **Water content analysis**
  - To measure the water content in the bio-oil.

- Water content of bio-oil can be determined by using a Karl Fischer Titrator.

- **Ash content analysis (Proximate analysis)**
  - To measure the total amount of minerals present within the bio-oil.
  - Bio-oil id heated in furnace for 3 hours with the temperature of 700 °C.
  - The ash content of bio-oil can be determined by equation:

$$\text{Ash content} = \frac{W_{ash}}{W_{Bio\text{-}oil}} \times 100\ \%$$

- **Calorimetry analysis**
  - To measure the amount of energy released when the bio-oil is completely combusted under specified conditions.
  - Calorific value of bio-oil can be determined by using a Bomb Calorimeter.

- **Elementary analysis**
  - To determine the composition of carbon, hydrogen, oxygen, sulfur and nitrogen in the bio-oil.
  - The composition of the bio-oil can be determined by using a CHNS analyzer.

CHAPTER 4

4. RESULT AND DISCUSSION

4.1 Biomass feedstock characterization

Oil palm fronds (stem part) a waste of a palm oil mill were used in this work. The result of *proximate analysis, elemental analysis and calorific value of oil palm frond are listed* in this section. At the first stage before the experimental works, the oil palm stem for fractions size 0.15 – 0.5mm have been analyzed to determine their properties using the techniques that have been explained in Chapter 3.

4.2 Data Analysis

The feedstock has been characterized and the basic characteristics are listed in the table below.

Table 5: The properties and characteristic of feedstock (oil palm stem)

Property	Value
Diameter [mm]	0.15 – 0.5
Moisture [wt %]	7.56
Calorific value [MJ/kg]	17.78
C [wt %]	41.965
H [wt %]	5.412
N [wt %]	1.0775
Ash [wt %]	2.72

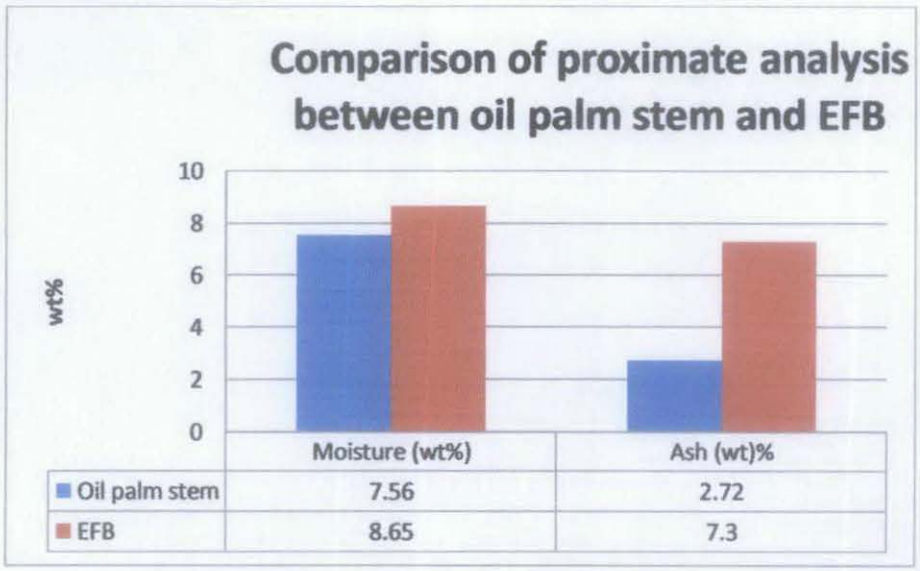

Figure 7: Graph comparison of proximate analysis between oil palm stem and EFB

According to the graph above, it shows that moisture content of oil palm leaf is less than the moisture content of EFB(empty fruit bunch). Less moisture a feedstock means more dry the feedstock. Therefore, the duration of pyrolysis process for feedstocks that have high moisture content is longer because the feedstocks take more time to evaporate compared to the feedstocks that have less moisture content. Other than that, high moisture content in the feedstocks will lead to high water content inside the bio-oil. Therefore, oil palm stem has possibility to produce bio-oil with less water content and the pyrolysis process will take less time to produce bio-oil. The moisture content (water) that is produced in the pyrolysis reaction together with any water contained from the biomass feedstock. The amount of water in the product also depends on the process parameters including the extent secondary reaction or cracking and the temperature of the products gases leaving the liquid collection system. Water is important in many ways as; higher water content usually reduced viscosity, improves stability but reduces calorific value of bio-oil.

Ash content analysis gives the ash (mineral) in the sample of oil palm stem and leaf. Two samples of stem were taken each and weighted around 0.5 g was put in suitable vessel was ignited and allowed to burn until only ash remained. The ash content for oil palm stem 0.15 – 0.5mm was based on ASTM E 1755-95.

Based on one journal [14], they discovered that it is generally accepted that ash, and particularly potassium, is catalytically active and favours secondary reactions leading to a reduction in organics yield, and corresponding increases in reaction water, gas and char yields. Therefore, less the ash content in a feedstock will result in produce more bio-oil and secondary reaction should be avoided for the production of liquid.. Based on the Figure 7, oil palm stem has possibility to maximize the liquid yield compared to EFB.

4.2.1 Calorimetry Analysis

The calorific value of oil palm stem and leaf 0.15 – 0.5mm was determined using a bomb calorimeter. Table 6 the results of calorimetry analysis for oil palm fond (stem and leaf) and comparison of calorific value for oil palm frond with EFB from literature review.

Table 6 : comparison of calorific value for oil palm frond with EFB

Feedstocks	Calorific Value (MJ/kg)
Oil palm stem (0.15 – 0.5mm)	17.78
EFB	16.80

From the results, oil palm stem has higher calorific value than EFB (empty fruit bunch). The higher the calorific value of a feedstock, the more potential it can to be used as fuel. According to the table 6 above, the calorific value of oil palm stem is higher than calorific value of EFB .Therefore, oil palm stem has high potential to be used as fuel.

4.2.2 Elementary Analysis

The elemental analysis provides the chemical composition of the oil palm stem in elemental terms and is used to determine the combustion air requirement, flue losses and likely emission levels. From the elementary analysis, it was found that oil palm stem

contained 41.97% of carbon, 5.41 of % hydrogen, 1.08 % of Nitrogen and 48.52% of Oxygen. As referred to the graph in Figure86, the percentage of carbon, hydrogen and nitrogen in oil palm stem is about similar with the percentage of carbon, hydrogen and nitrogen in EFB [12] just the percentage of Oxygen is slightly higher compared to EFB.

Table 7: Result of elementary analysis for oil palm stem

Feedstocks	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)	Ash (%)
Oil palm stem (0.5 – 1mm)	41.965	5.412	1.0775	0.31	48.5155	2.72

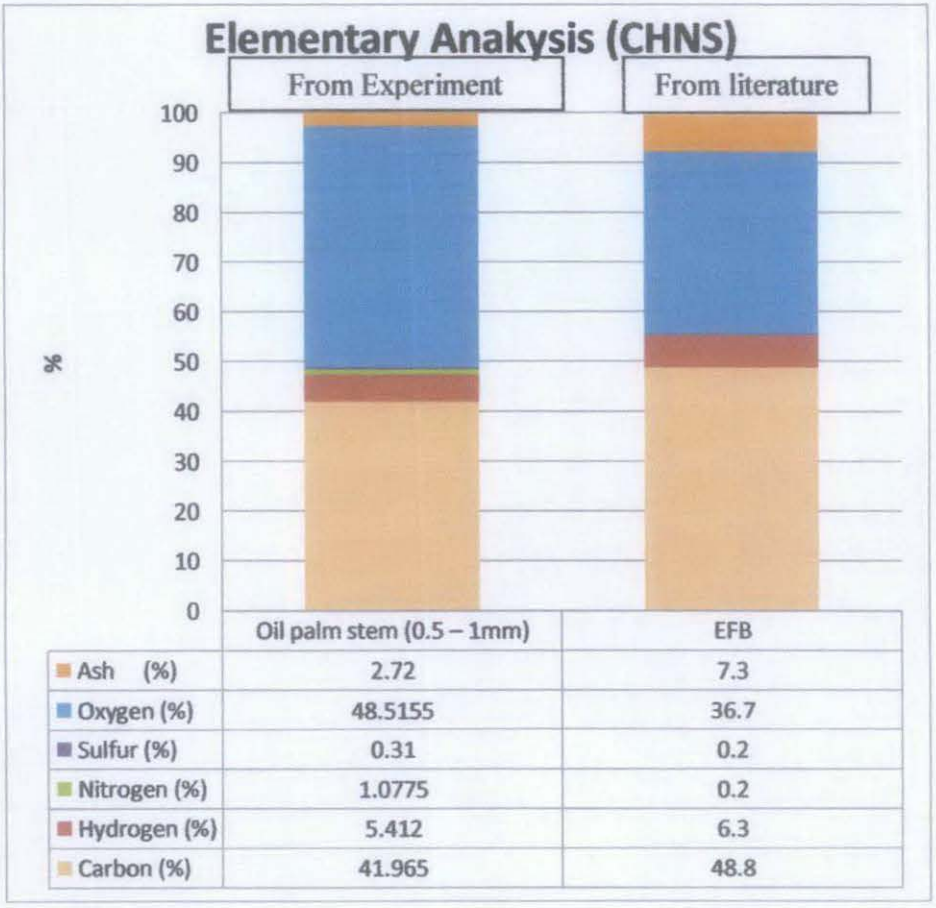

Figure 8: Comparison of elementary analysis for oil palm stem with EFB [2]

4.3 Fast Pyrolysis product (Bio-oil)

Table below present the pyrolysis condition and product yield from the experiment. Pyrolysis temperature use in this experiment was 450°C Pyrolysis temperature and vapor residence time were the most important parameter affecting the product yield. Bio-oil yield of only 11.72% produced in this experiment due to several factors. The vapor residence time was expected to have the largest effect on the pyrolysis yield and chemical composition for this experiment. Six fractions of bio-oil samples were collected from the six condensers (see Fig.5), respectively. The total bio-oil yield was 11.72 %, bio char was 82.28% and gas was 5.99%.

Table 8: Pyrolysis condition and product yield

Bed temperature(^{0}C)	**450**
Fluidizing medium	Nitrogen
Feedstock size (mm)	0.15-0.5
Gas flow rate (L/min)	22
Feed rate (kg/h)	0.5
Bio-oil yield (wt%)	11.72478
Bio-Char yield (wt%)	82.282
Gas yield (wt%)	5.99322

Table 9 : Bio-oil mass and yield% from each condenser

Bio oil	**Mass (g)**	**Yield %**
1st condenser	31.2655	53.33234
2nd condenser	13.2976	22.6829
3rd condenser	6.0561	10.33043
4th condenser	4.0822	6.963372
5th condenser	2.5867	4.412364
6th condenser	*1.3358*	2.278593
Total	**58.6239**	**100**

4.4 Bio-oil Characterization

The bio-oils obtained at temperature 450°C and particle size of 0.15-0.5mm was characterized with respect to each condenser characteristics as shown in table 5. The water content of bio-oils varied between 24% to 82% depending on condenser. The bio-oil sample from fifth and sixth condenser show no calorific value when test it with bomb calorimeter. This tendency may be attributed to the fact that the fifth and sixth bio-oils consist of a major amount of watery phase and a minor amount of oily phase.

Table 10: Characteristic of bio-oil

	Bio-oil					
Property	**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**
Water / Moisture [wt %]	32.6	24.2	37.2	41.3	81.5	40.3
Calorific value HHV [MJ/kg]	14.0	16.2	12.4	-	-	12.7
C [wt %]	35.3	39.8	37.6	33.5	17.5	20.1
H [wt %]	6.67	7.98	7.6	8.6	8.2	8.8
N [wt %]	1.02	1.93	0.7	1.3	0.9	0.9
Ash [wt %]	0.12	0.25	0.40	0.49	0.78	2.74
Yield (wt% bio-oil)	53.3	22.7	10.3	6.96	4.41	2.28

The water content that is produced in the pyrolysis reaction together with any water contained from the biomass feedstock. The amount of water in product also depend on The amount of water in the product also depends on the process parameters including the extent of secondary reaction or cracking and the temperature of the product gases leaving the liquid collection system. Water is important in many ways as higher water content usually reduce viscosity, improves stability but reduces calorific value of bio-oils. Results plotted in Fig. 10 shows the relationship between water content and calorific value of the bio-oil. The ash content in the bio-oils varied from 0.12% to 2.74%. Ash can result from oil or water-soluble metallic compounds or extraneous solid such as dirt and rust. As the carbon content in the bio-oil is lower, the value of calorific value also is lesser in the bio-oil from fifth condenser (see figure 5). This mean that high water content in combination with lower carbon content gives poor calorific value.

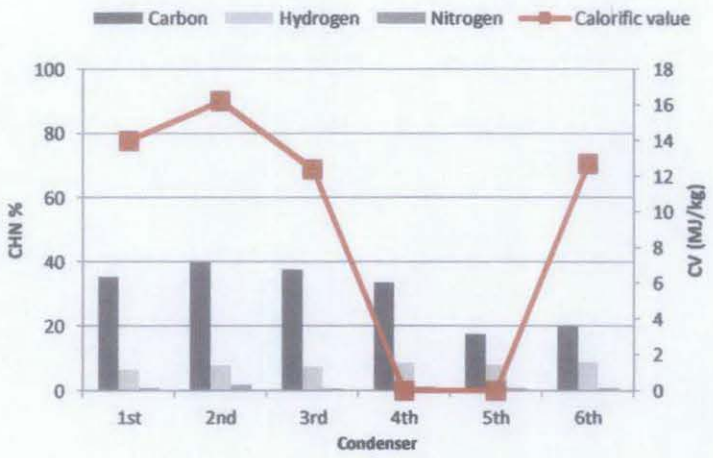

Figure 9: CHN contents and calorific value (CV) for bio-oil samples

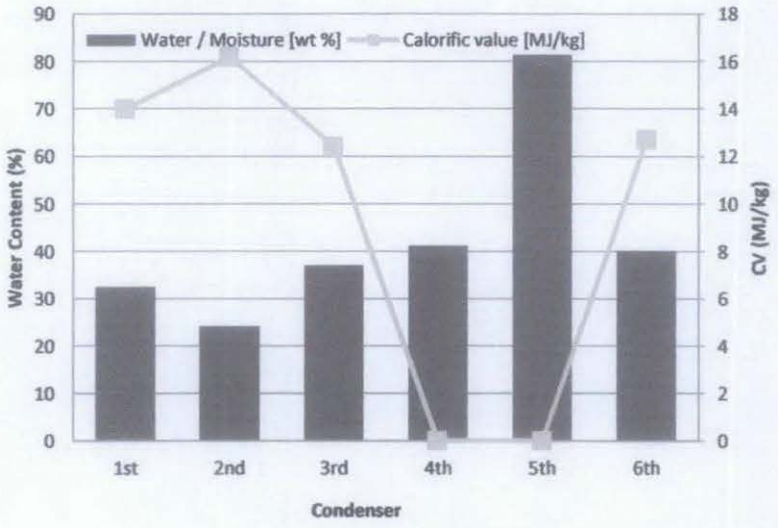

Figure 10: Water content and calorific value (CV) for bio-oil samples

4.5 Vapor Residence Time

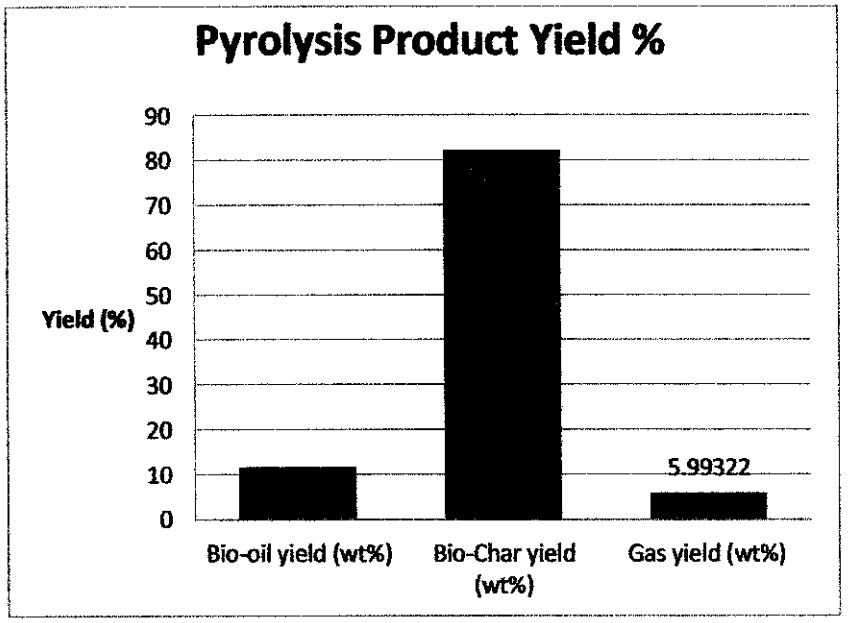

Figure 11 : Pyrolysis product yield using fluidize bed reactor

Graph above shows the result of bio-oil produced using 500g/h feeding rate of oil palm stem biomass. The experiment run with reactor temperature of 450 ^{0}C and Nitrogen gas flow was 1.32m3/h. Bio-oil yield produced was lower than bio-char yield. It may be due to more secondary reaction occurred in the bio oil produced as the residence time was high (about 7 seconds). The residence time of the pyrolysis determines the time available for vapor phase reactions, affecting the gas and bio-oil yields. At lower gas flows rates, the residence time of the vapors in the reactor increases, which supports the possibility of secondary reactions such as thermal cracking, repolymerization, and recondensation, leading to a decrease in the bio-oil yield. For a fixed temperature and reactor volume, the residence time is determined by volumetric flow rate of the fluidizing medium and pyrolisis vapor. Hyun Ju Park reported in one journal about clean bio oil production from fast pyrolisis of sewage sludge, the increasing flow rate of nitrogen was yielded larger amounts of bio-oil due to reduced vapor residence time when doubling the feed rate to 5g/min led to 45.1 wt %. In this experiment, the vapor residence is determined by find the superficial velocity at 450°C. Length of bed used in

this pyrolysis process was 71.5cm and had been divided with the value of superficial velocity and finally residence time got was 7 seconds.

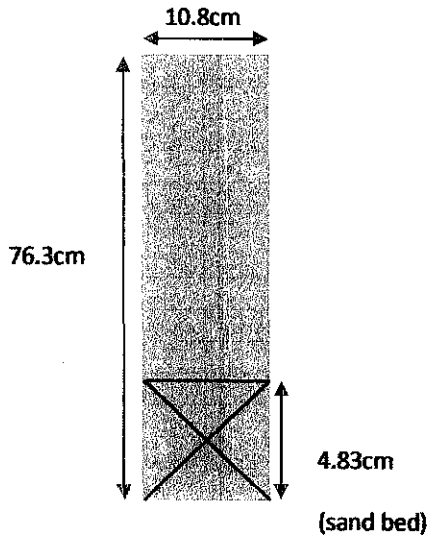

Figure 12 : Length and diameter of fluidized bed reactor

Area = pai /4*10.8^2

=91.6 cm^2

Nitrogen flowrate use for this pyrolysis process is 22 L/min (22000cm^3/min), and by dividing with area, the superficial velocity at 25C is equal to 4.00 cm/s. Using the correction factor the superficial velocity at 450°C got is 9.72 cm/s. Residence time is calculate by :

$$\text{Residence time} = \frac{(\text{height of reactor} - \text{height of sand bed})}{Superficial\ velocity\ at\ 450^{\circ}C}$$

$$= \frac{(76.3cm - 4.83cm)}{9.72cm/s}$$

= 7 second

4.6 Minimum Fluidization Velocity, u_{mf}

U_{mf} may be determined by measuring the pressure drop through a bed of particles as a function of the superficial gas velocity. At U_{mf}, the weight of the bed is fully supported by the flow and the pressure drop becomes constant.

The experiment were carried out with the gas velocity above the minimum-bubbling fluidizing velocity(U_{mf}), which was calculated to be 2.264 cm/s using Wen and Yu equation.

$$U_{mf} = \frac{\mu}{d_p \rho_f} Re_{mf} \quad (1)$$

$$Re_{mf} = \sqrt{C_1^2 + C_2 Ar} - C_1 \quad (2)$$

Wen and Yu found that C_1=33.7, C_2=0.0408 in a wide experimental range and substitute the value in the equation (2):

$$Re_{mf} = \sqrt{33.7^2 + 0.0408 Ar} - 33.7 \quad (3)$$

While the equation for Archimedes number is :

$$Ar = \frac{d_p^3 \rho_f (\rho_p - \rho_f) g}{\mu^2} \quad (4)$$

Where ;

g= 9.81 [m/s^2]

d_p= particle size [m]

ρ_f= Fluid density [kg/m^3]

ρ_p= particle density [kg/m^3]

μ = Fluid viscosity [kg/m^2]

Properties of nitrogen at 450^{0}C need to be found in order the get the exact value of minimum fluidization velocity at the operated temperature. Viscosity of nitrogen gas is equal to 3.4209*10^{-5} kg/m.s while the density of Nitrogen gas (ρ_f) is calculated by:

ρ_f = m/V

$$= \frac{molecular\ weight[g]}{22[L]*((T[^0C]+273.2/273.2))}$$

$$= \frac{28.01}{22x\left[\frac{(450+273.2)}{273.2}\right]}$$

$$= 0.480964\ [kg/m^3]$$

The size of biomass (d_p) use in this experiment was 0.15- 0.5mm and the average of this size were taken in order to calculate Archimedes number that is 0.325mm. The density of the biomass was determined using pycnometer. The picture of pycnometer is shown in picture below. The density of biomass (ρ_p) got is 1093.8 kg/m^3.

Figure 13: Pycnometer used to determine the density of biomass

By substitute the value; d_p =0.000325 m, ρ_f= 0.480964 kg/m3, ρ_p= 1093.8 kg/m,^{3} and μ = 3.4209 x 10^5 kg/m.s in equation(4) the value of Archimedes Number at 450°C was 151.3179. The value of Ar number got is then substituted in equation (3) to get the value of Re_{mf} .

$$Re_{mf} = \sqrt{33.7^2 + 0.0408(151.3179)} - 33.7$$

$$= 0.1114207$$

The last step is to find the minimum fluidizing velocity, substitute Re_{mf} value in equation (1):

$$U_{mf} = \frac{\mu}{d_p \rho_f} Re_{mf}$$

$$= \frac{3.4209x10^{-5}}{0.000325\ x\ 0.480964}\ x\ 0.1114207$$

= 0.02264 m/s

=2.264 cm/s

Fluidizing biomass particle is challenging due their irregular size, shape and density Understanding the influence of these particular characteristic on the fluidized bed hydrodynamics is important. (Zhong et al. 2008) studied effect of particle size, density, and shape on the minimum fluidization velocity using wood ships, and mung beans. The minimum fluidization velocity also constitutes a reference for evaluating fluidization intensity when the bed is operated at higher gas velocities (Zhong et al. 2008). In general, U_{mf} is a function of particle properties/geometry, fluid properties, and bed geometry.

The experiment must be carried out at a gas velocity above the minimum bubbling fluidizing velocity so it will have enough drag force needed to attain solid suspension in the gas phase. In this experiment, the nitrogen flowrate was 22 L/min or equal to 22000 cm^3/min. superficial velocity at 450 °C was calculated by dividing flowrate with area of reactor. The value of superficial velocity calculated was 9.72 cm/s which were above the minimum fluidizing velocity that was 2.264 cm/s.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Fast pyrolysis process of oil palm stem has been successfully performed using fluidized bed reactor. The bio-oil yield of 11% was obtained at reaction temperature of 450 °C with the particle size of 0.15 – 0.5 mm. The highest calorific value and the lowest water content of the bio-oil obtained were 16.2 MJ/kg and 24.2wt%, respectively, which drawn from second condenser. The experiment was carried out at a gas velocity above the minimum fluidizing velocity u_{mf} which was approximately 2.3cm/s. The chemical characterization and calculation of residence time showed that the condition of pyrolysis in this experiment is not favorable in producing bio-oil, however effective to produce bio-char.

REFERENCES

Agblevor, F.A.; Besler, S.; and Wiselogel, A.E., 1995. Fast Pyrolysis of Stored Biomass Feedstocks. Energy and Fuels. 9: 6.

Bridgwater, A.V, Czernik, S., and Piskorz, J.,2002. The status of biomass fast pyrolysis in Fast Pyrolysis of Biomass: A Handbook, vol 2(ed. A. V. Bridgewater), CPL Press, Newbury, pp.1-22

Dorian J.P., Franssen H.T. and Simbeck D.R..,2006. Global challenges in energy, Energy Policy 34, pp. 1984–1991

Hyeon Su Heo, Hyun Ju Park, Young-Kwon Park, Changkook Ryu, Dong Jin Suh, Young-Woong Suh, Jin-Heong Yim, Seung- Soo Kim., 2010. "Bio-oil production from fast pyrolysis of waste furniture sawdust in a fluidized bed." Bioresource technology 101 Suppl :S91-96.

Horne and Williams, Horne P.A., Williams P.T.., 1996 "Upgrading of biomass-derived pyrolytic vapours over zeolite ZSM-5 catalyst: effect of catalyst dilution on product yields" Fuel, 75, pp. 1043–1050

Jun Shen, Xiao-Shan Wang, Manuel Garcia-Perez, Daniel Mourant, Martin J Rhodes, Chun-Zhu Li., 2009. Effects of particle size on the fast pyrolysis of oil mallee woody biomass, Fuel, Volume 88, Pages 1810-1817.

Mahlia, T.M.I., M.Z. Abdulmuin, Alamsyah T.M.I and Mukhlishien. D., 2001. "An alternative energy source fom palmwaste industry for Malaysia and Indonesia," Energy Conversion and Management 42: 2109-2118.

Malaysian palm oil board. Online at http://www.mpobgovmy.

Manoj Khandelwal, Singh. T.N., 2010. Prediction of macerals contents of Indian coals from proximate and ultimate analyses using artificial neural networks, Fuel, Volume 89, Issue 5, Pages 1101-1109.

Meier D, and Faix. O., 2006. State of the art of applied fast pyrolysis of lignocellulosic materials—a review, Bioresource Technology 68, pp. 71–77.Ranu, B C.; Jana, R. Eur. J. Org. Chem., 3767-3770

Mohammed, M.a.a., 2011. "Hydrogen rich gas from oil palm biomass as a potential source of renewable energy in Malaysia." Renewable and Sustainable Energy Reviews 15:1258-1270.

Park, Young-kwon, Jong-ki Jeon, and Seungdo Kim. 2004. "Bio-oil from rice straw by pyrolysis using fluidized bed and char removal." Water 49:800-801.

Sumathy K., M. Ni, M.K.H. Leung, and D.Y.C. Leung., 2006. Potential of renewable hydrogen production for energy supply in Hong Kong, International Journal of Hydrogen Energy 31, pp. 1401–1412

Westermann P., Jãrgensen B., Lange L., Ahring B.K. and Christensen C.H., 2007. Maximizing renewable hydrogen production from biomass in a bio/catalytic refinery, International Journal of Hydrogen Energy 32, pp. 4135–4141

Wikipedia. The free encyclopedia: pyrolysis oil. Available from: http://en.wikipedia.org/wiki/Bio-oil

Zhong, Jin. B W., Zhang. Y., Wang. X. and Xiao, R., 2008. "Fluidization of biomass particles in a gas-solid fluidized bed," Energy & Fuels, 22(6): 4170-4176.